Ohio State University

Two-Stage Catalytic Reduction of NOx

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COOPERATIVE AGREEMENT DE-FC26-02NT41608

Awarded (10/1/02, 36 Month Duration)

$760,321 Total Contract Value ($600,930 DOE)

Project Objectives

- Develop a two-stage catalytic system capable of reducing NO with methane in excess oxygen conditions
  - **Formulate and synthesize NO oxidation and NO_2 reduction reactions**
  - **Examine catalytic activity through steady-state reaction experiments.**
  - **Develop understanding of catalyst behavior by use of a wide array of characterization techniques.**
  - **Quantify system performance**
  - **Project the design economics for large bore natural gas engines.**

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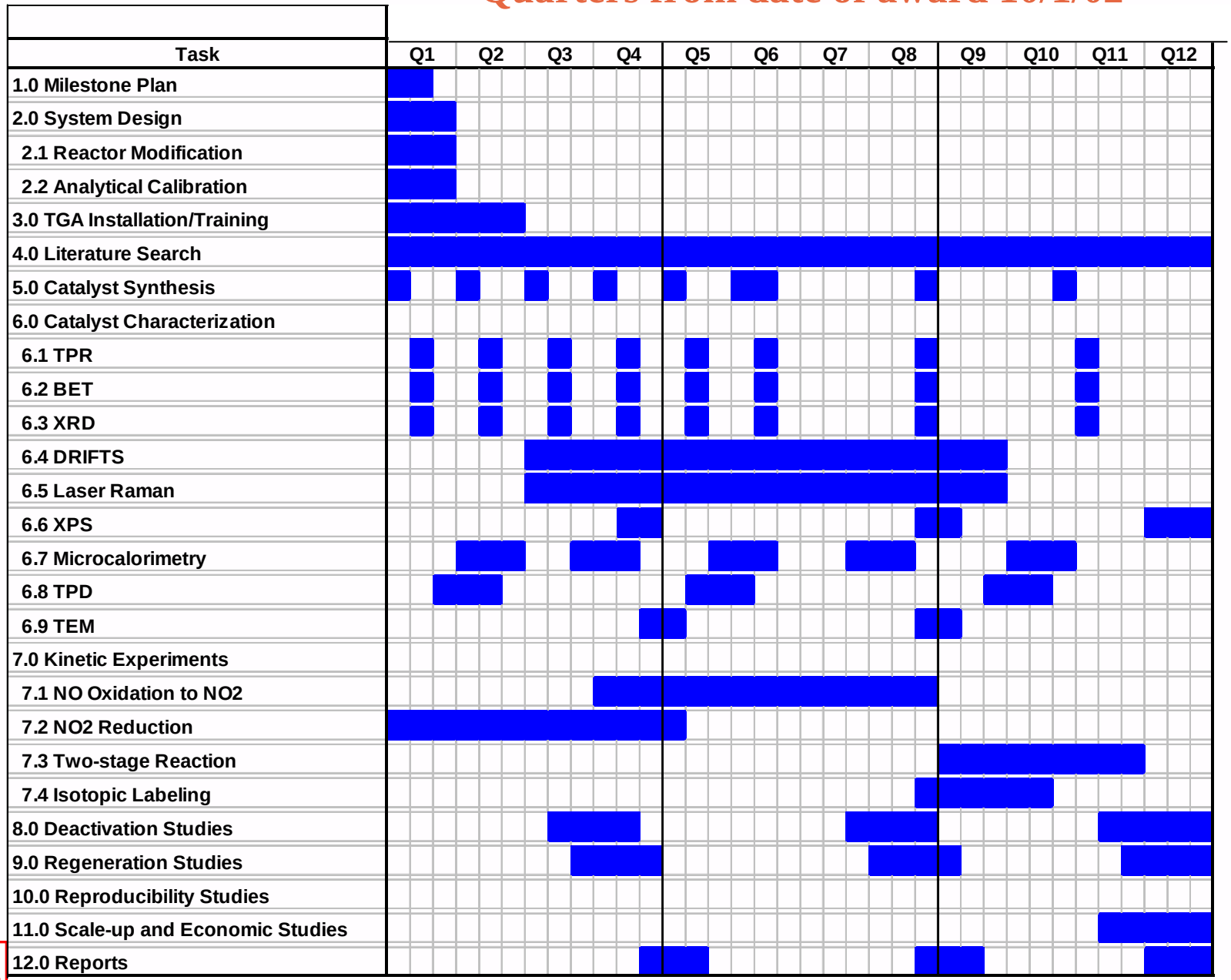
Quarters from date of award 10/1/02



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Time Table

Accomplishments to date

- **Expanding literature review.**
- **Prepare Project Milestone Plan with student participation**
- **Selection and purchase of:**
  - Microcalorimetry system – Seteram TGA/DSC-111
  - Micro GC – Varian CP-4900
- **Installation of and training on new microcalorimetry and micro-GC equipment.**
- **Modification and calibration of experimental reaction system.**
- **Initial formulation and synthesis of oxidation and reduction catalysts.**
- **Proof of concept experiments for NO_2 reduction reaction.**
- **Proof of concept experiments for NO oxidation reaction.**
- **Initial characterization of catalysts.**

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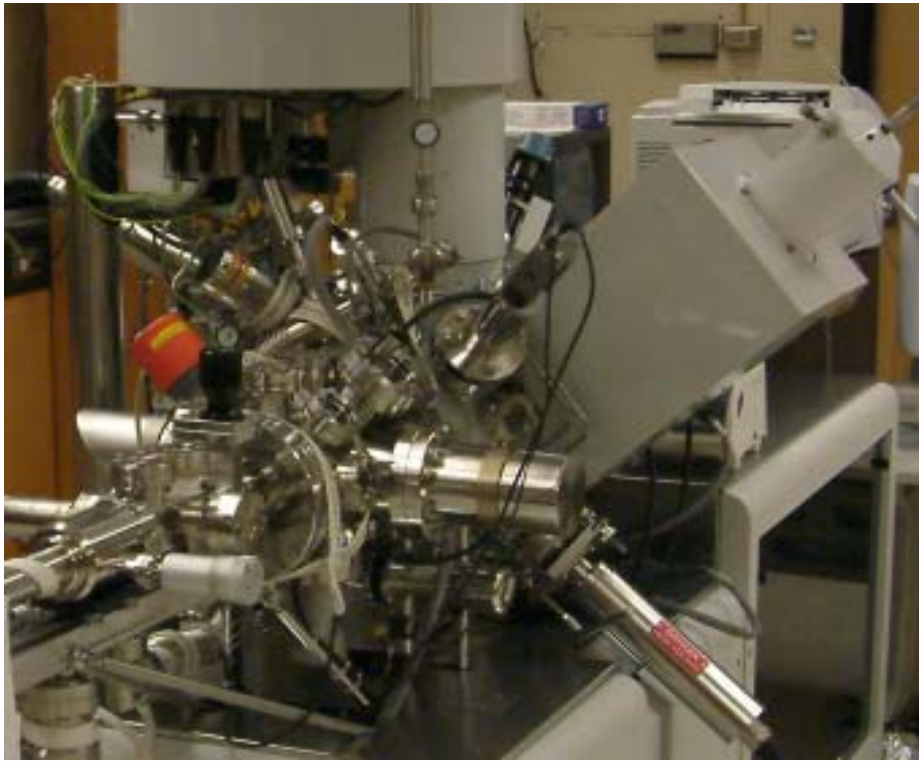
Technical Approach and Results



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Two-Stage Catalytic Reduction Concept

- Oxidation of NO to NO_2 over an oxidation catalyst
- Reduction of NO_2 to N_2 and H_2O over a reduction catalyst using CH_4 as the reducing agent
- NO_2 is a stronger oxidizing agent, and hence should be more easily reduced.
- NO_2 reduction can more favorably compete with O_2 for CH_4.

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Two-Stage Catalytic Reduction Concept

- **Excess oxygen conditions will favor NO to NO_2 oxidation.**
- **NO oxidation is thermodynamically limited at high temperatures.**
- **Requires highly active oxidation catalysts to reach high conversion at low temperatures.**

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Work plan

- **Catalyst formulation and synthesis**
  - **Highly active NO oxidation catalysts**
  - **NO_2 reduction catalysts that can function at excess oxygen conditions**
- **Catalyst characterization**
  - **Physical, structural and molecular characterization of the catalysts**
  - **In-situ characterization under reaction conditions**
  - **Techniques:**
    - **BET surface area, pore size distribution**
    - **X-ray Diffraction**
    - **X-ray photoelectron spectroscopy**
    - **Electron microscopy (TEM, SEM)**
    - **Temperature programmed reduction**
    - **Temperature programmed desorption**
    - **Diffuse reflectance FTIR spectroscopy**
    - **Thermogravimetry and microcalorimetry**
- **Steady-state reaction studies**
  - **NO oxidation and NO_2 reduction reaction studies**

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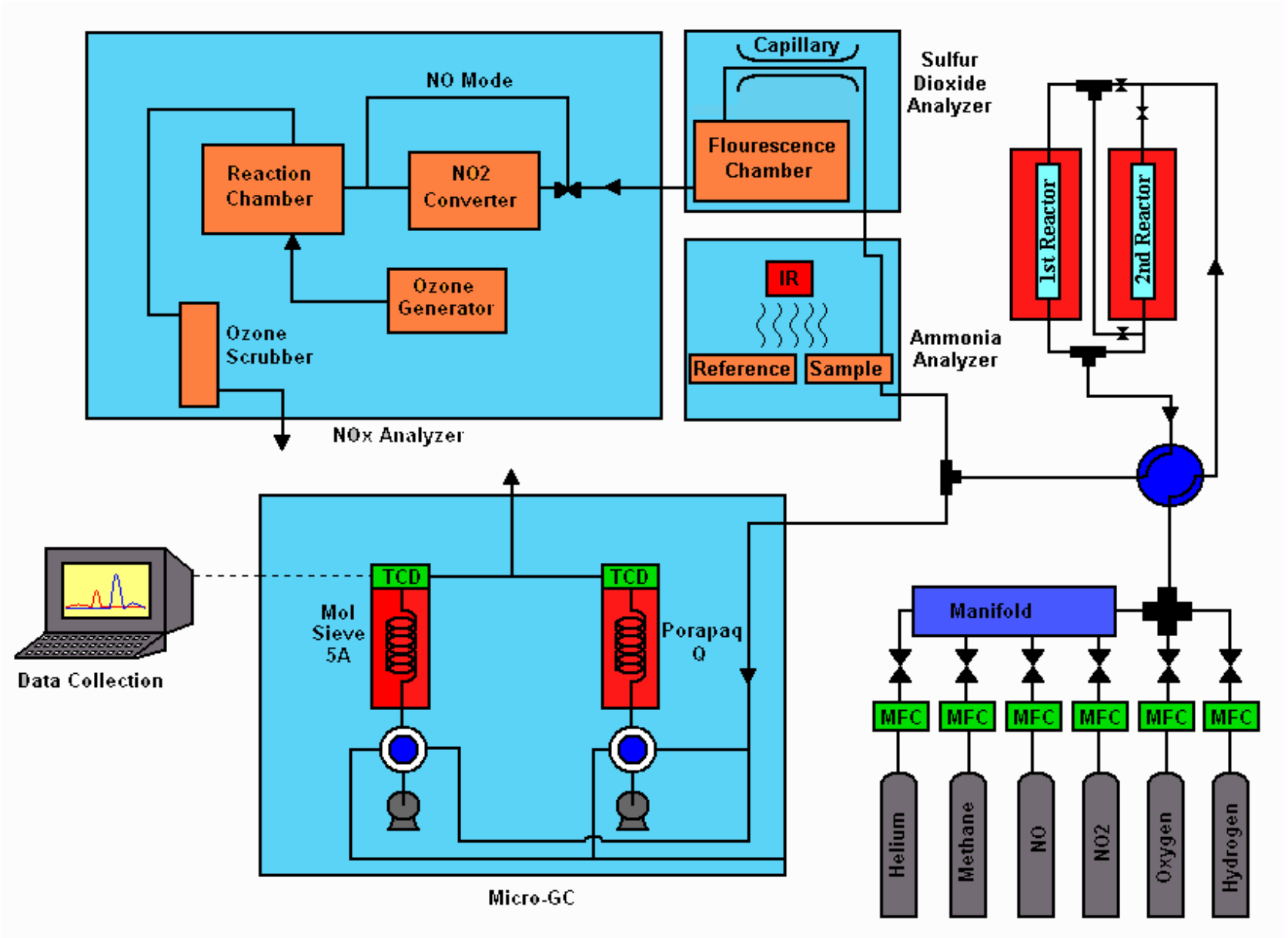

Reactor System

Analytical system

- Chemiluminescence NO_x analyzer
- Pulsed fluorescence SO_2 analyzer
- Infrared NH_3 analyzer
- Mass spectrometer (Isotopic labeling capability)
- Varian microGC
  - 10 ppm detection limit
  - 70 sec analysis time

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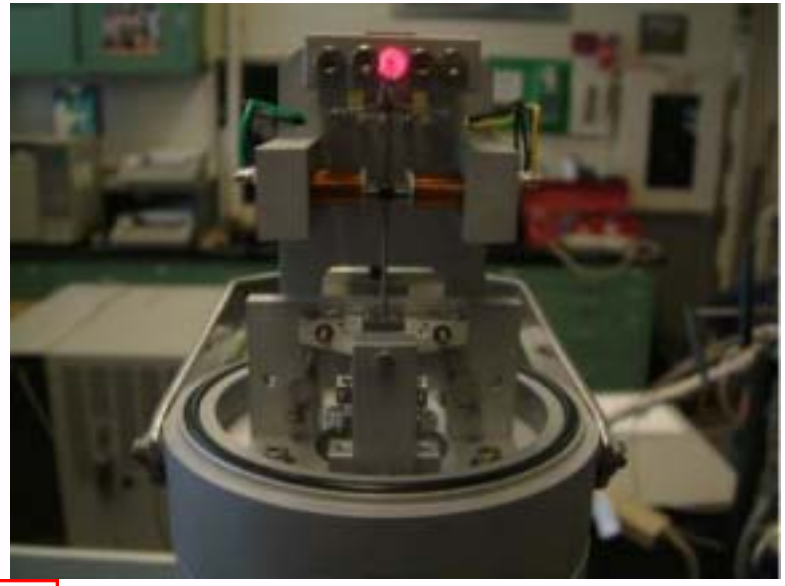
Thermogravimetry/DifferentialScanning Calorimetry (TGA/DSC)

Heats of adsorption, desorption, reaction

Thermogravimetric variations

Detection limits : 2μg, 5μW

Temperature range: -123 to 827°C



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Catalyst Synthesis: Sol-gel Chemistry

- Sol-gel chemistry allows materials to be mixed on an atomic scale by forming a colloidal suspension (sol) and gelation of the sol to form a network of solid skeleton filled with a solvent.

  - Hydrolysis: $H_2O + Ti\text{-}OR \rightarrow Ti\text{-}OH + R\text{-}OH$
  - Condensation: $Ti\text{-}OH + Ti^*ROH \rightarrow Ti\text{-}OH\text{-}Ti + ROH$

    $Ti\text{-}OH + Ti^*H_2O \rightarrow Ti\text{-}OH\text{-}Ti + H_2O$

    $Ti\text{-}OH + Ti\text{-}OH \rightarrow Ti\text{-}O\text{-}Ti + H_2O$

- The thermodynamics of these processes are highly dependent on
  - The strength of the entering nucleophile
  - The electronegativity of the metal
  - The partial charge and stability of the leaving group.

- The particle size, porosity, and surface area of the gel are strongly dependent on
  - pH
  - type of solvents
  - hydrolysis rate
  - water to precursor ratio
  - aging

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Initial Formulations for NOx Reduction Catalysts

Catalyst	Preparation	S.A. (m^2/g)
$2\%Pd/TiO_2$	Wet-impregnation	19
$2\%Pd/TiO_2$	Modified sol-gel	80
$1\%Ce/2\%Pd/TiO_2$	Wet-impregnation	12
$1\%Ce/2\%Pd/TiO_2$	Modified sol-gel	28
$1\%Gd/2\%Pd/TiO_2$	Modified sol-gel	79
$1\%La/2\%Pd/TiO_2$	Modified sol-gel	82
$1\%Yb/2\%Pd/TiO_2$	Modified sol-gel	66
$2\%Pd/AC\text{-}TiO_2$	Modified sol-gel	277
$1\%Gd/2\%Pd/AC\text{-}TiO_2$	Modified sol-gel	550

- Precursors: Palladium acetate, Titanium (IV) isopropoxide, Gadolinium nitrate, Cerium nitrate, Lanthanum nitrate, Ytterbium nitrate, Activated carbon
- Nitrogen is used as the adsorbate at liquid nitrogen temperature.
- The sample is degassed at 130 ^oC over night before the adsorption process is started.

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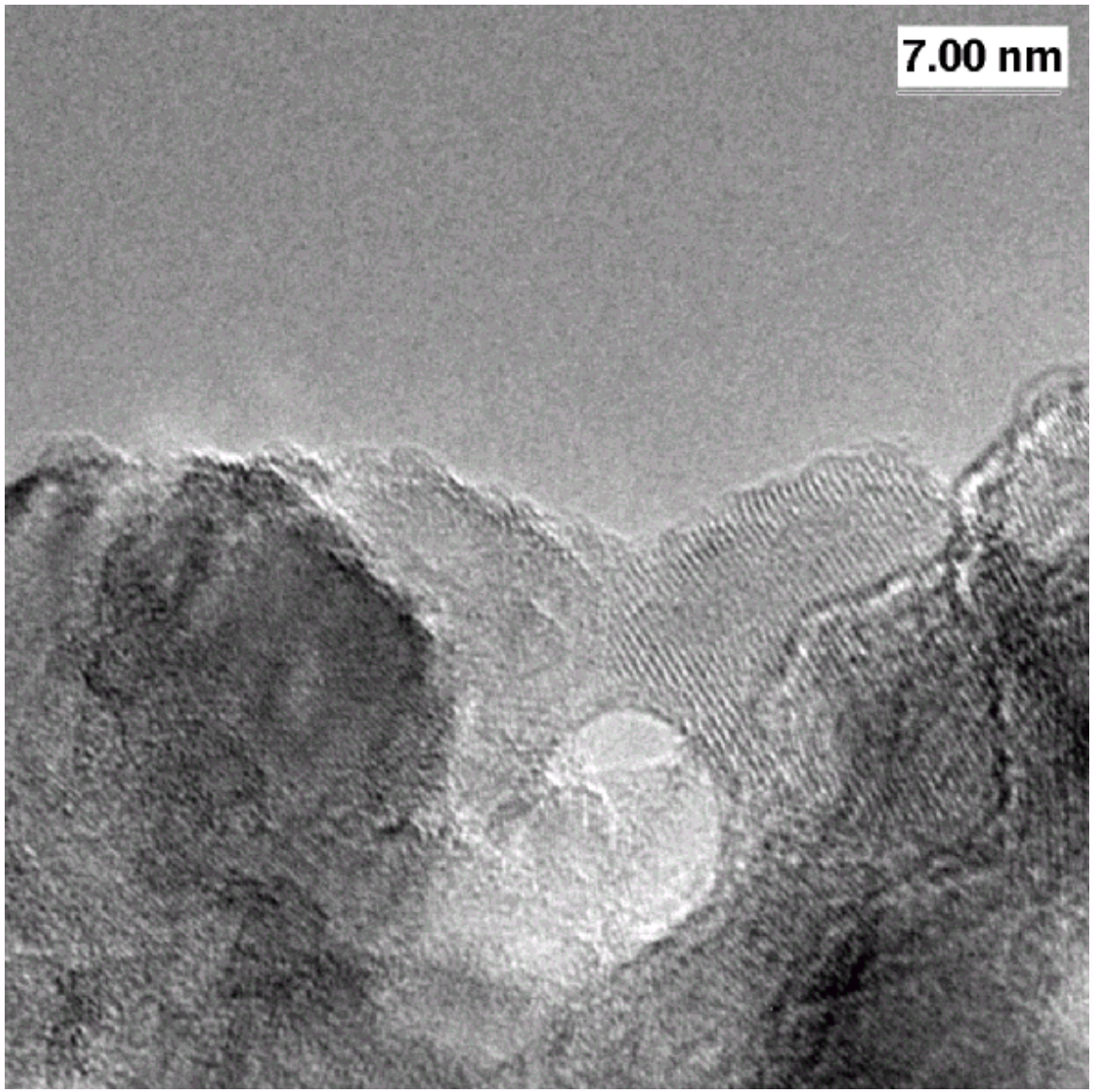
TEM image of Pd/TiO_2



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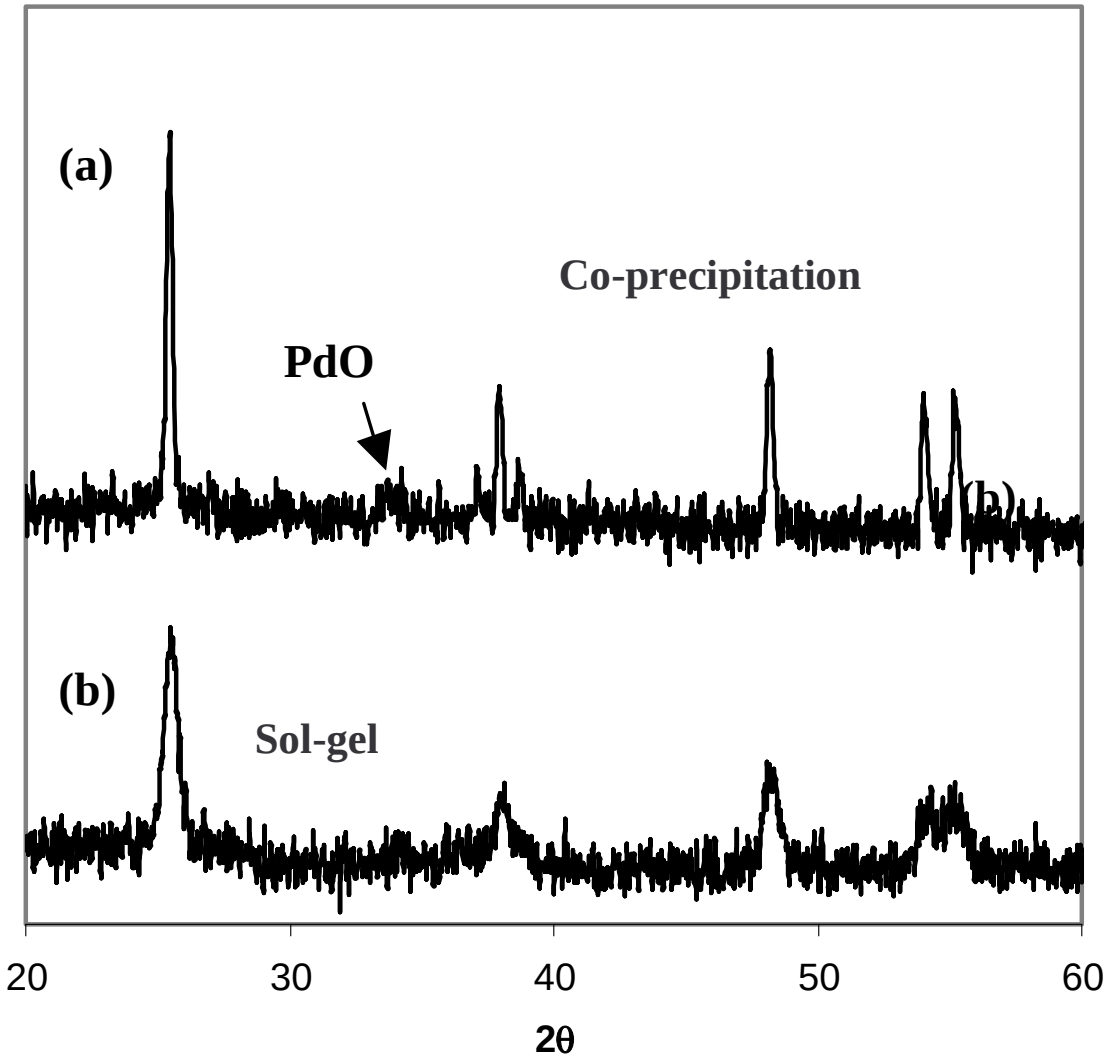
X-Ray diffraction patterns of oxidized Pd/TiO_2 samples



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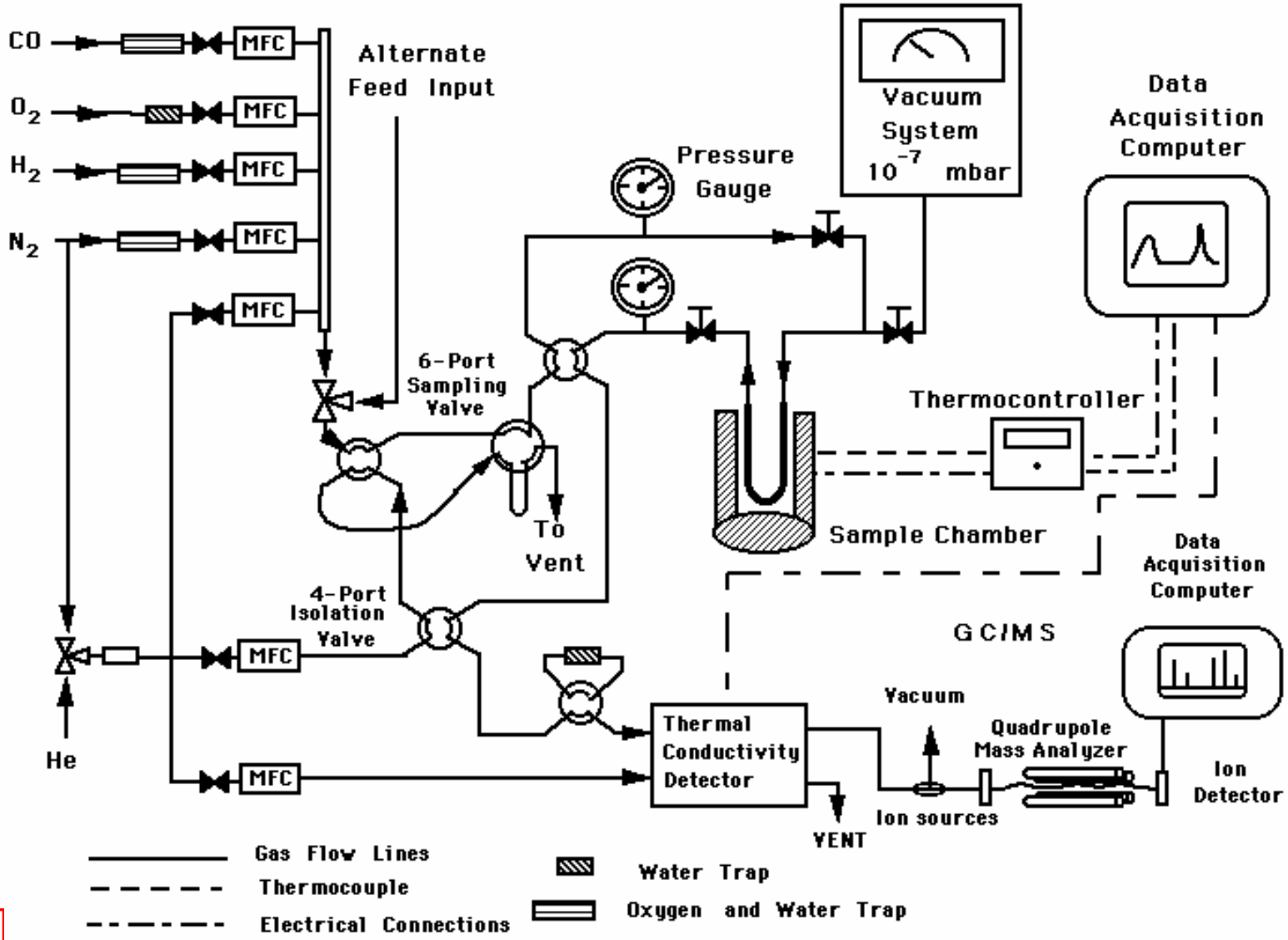
High-Vacuum Temperature-Programmed Reduction/Adsorption/Desorption System



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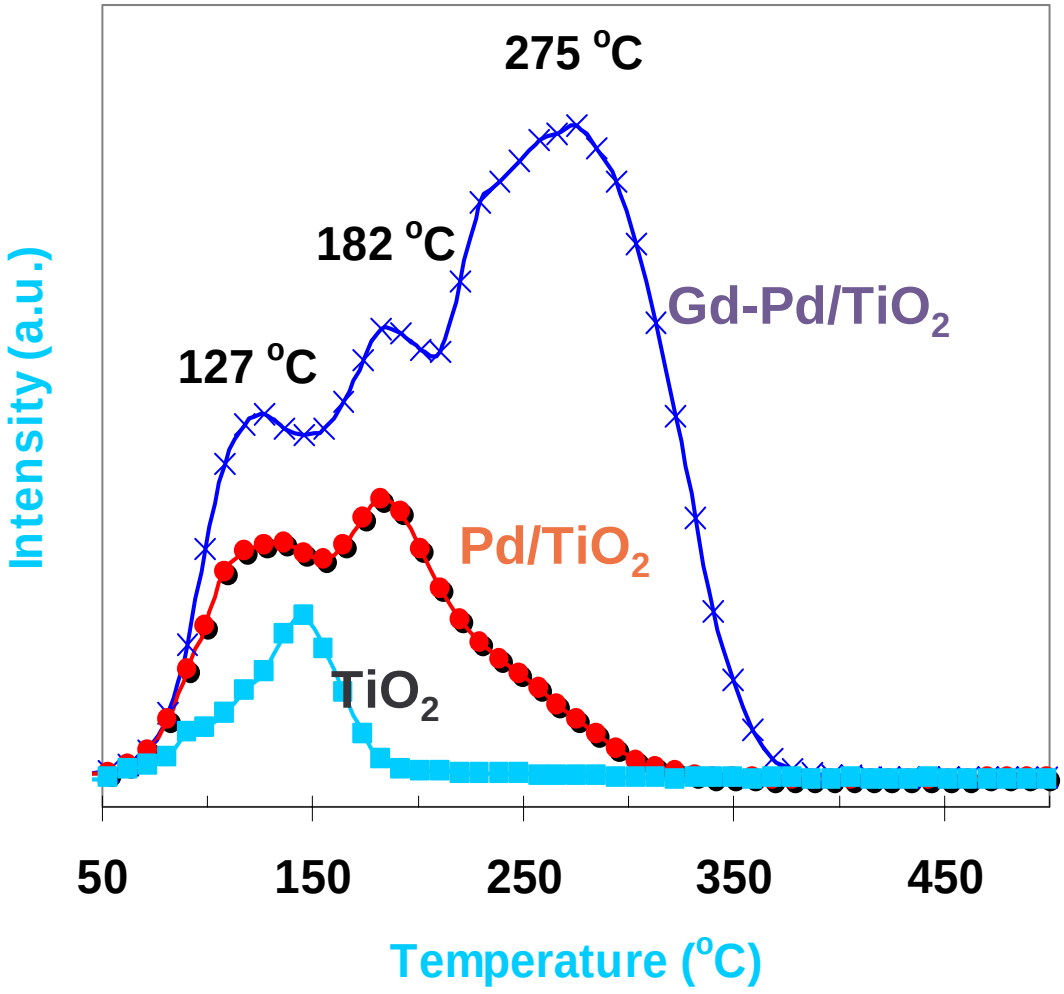
Temperature-Programmed Desorption of NO

In-situ Pretreatment

- Calcination: 10% O_2/He at 500 ^oC, 30 min.
- *In-situ* Reduction: 33% H_2/He at 200 ^oC, 30 min.
- NO adsorption: 5000 ppm NO, at room temperature, 1 hr
- **Temperature program**
  - Initial temperature: 25 ^oC
  - Ramp: 10 ^oC/min
  - Final temperature: 700 ^oC



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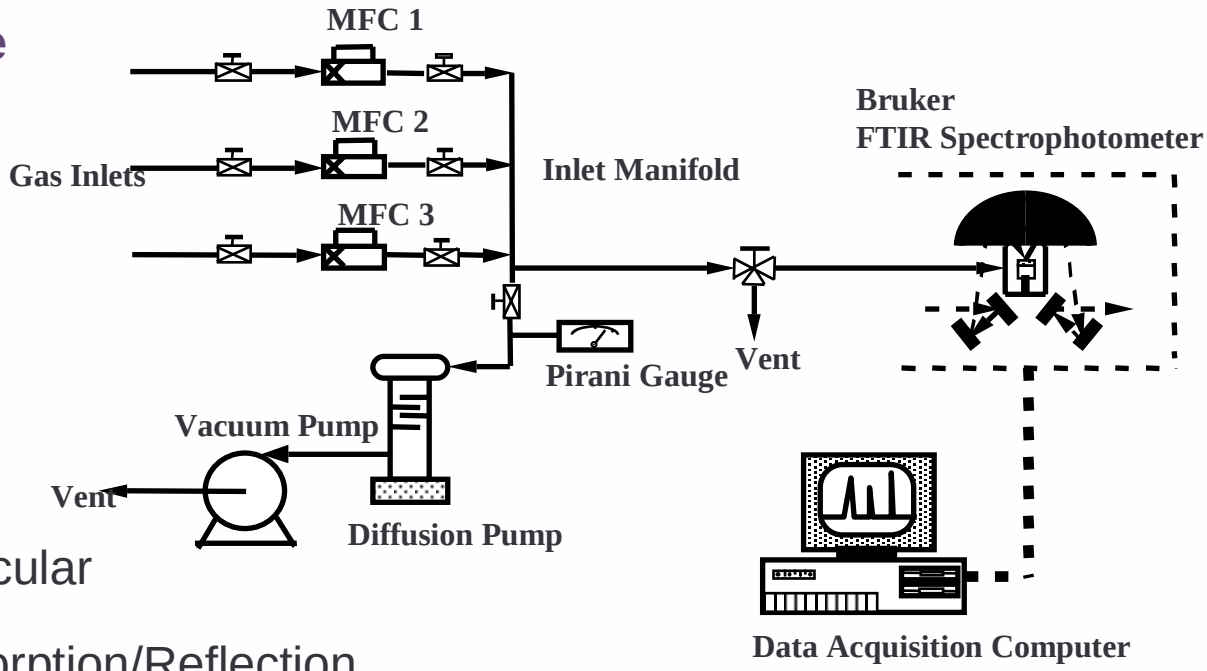
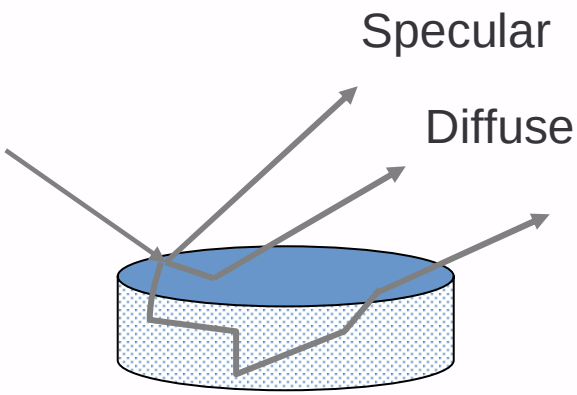
Diffuse Reflectance Infrared Fourier Transform Spectroscopy

- ***In-situ*** **DRIFTS gives information about adsorbed species on the catalyst surface.**
- **Ideal for powdered samples.**

Schematic of DRIFTS System





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In-situ DRIFTS

- Experimental parameters
  - Bruker IFS/66 Spectrometer
  - Mid IR range (400 to 4000 cm^{-1})
  - DTGS detector
  - KBr beam splitter
  - 1000 spectra averaged
  - 2 cm^{-1} resolution

- Adsorption experiments
  - NO adsorption followed by heating of the sample under He (TPD) to observe surface species

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NO-TPD over Reduced Pd/TiO_2

- A small band at 1751 cm^{-1} was observed at 27 ^oC and shifted to 1788 cm^{-1} with temperature in the presence of Pd. This region is characteristic of linearly adsorbed NO on Pd.
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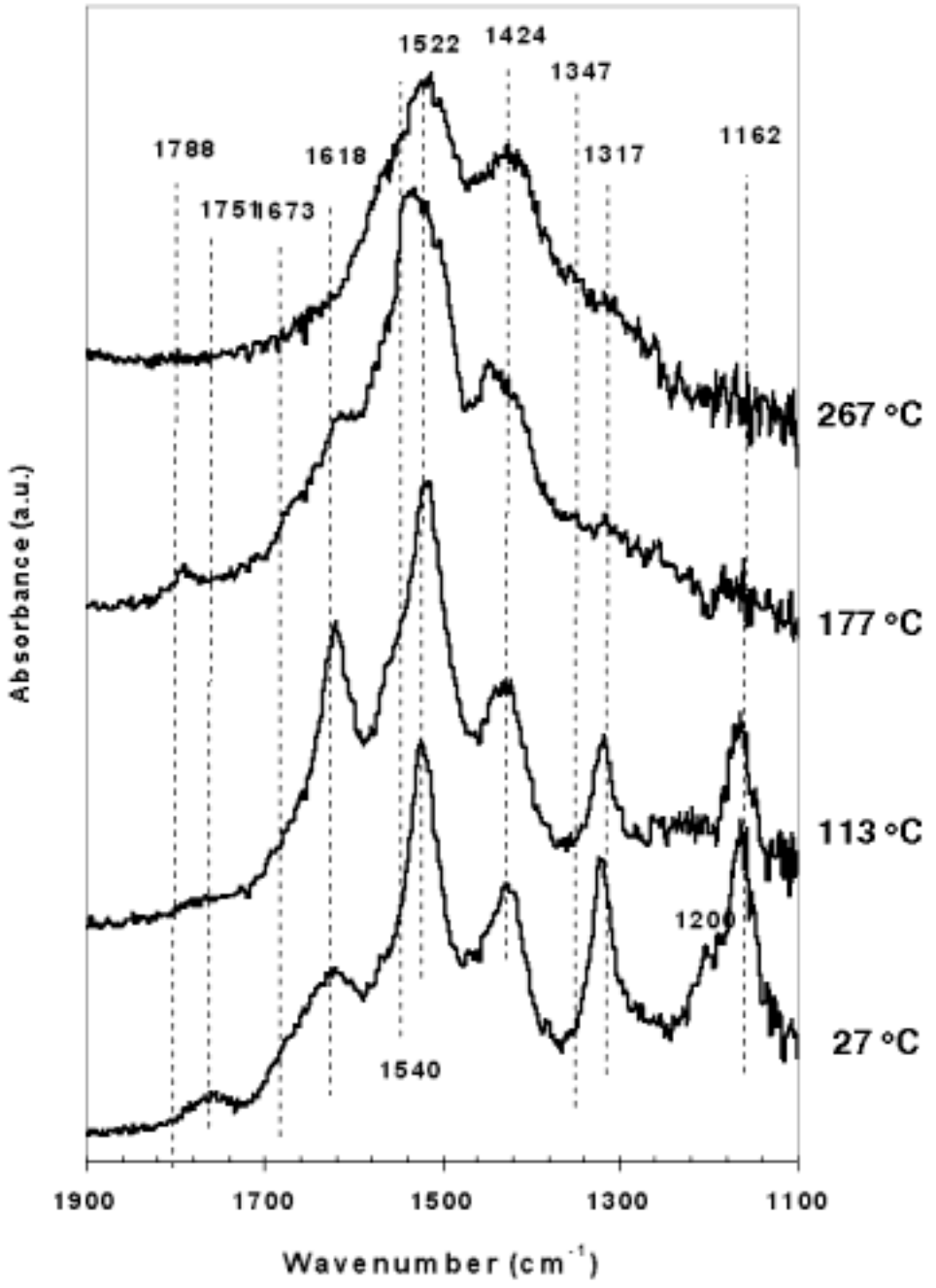

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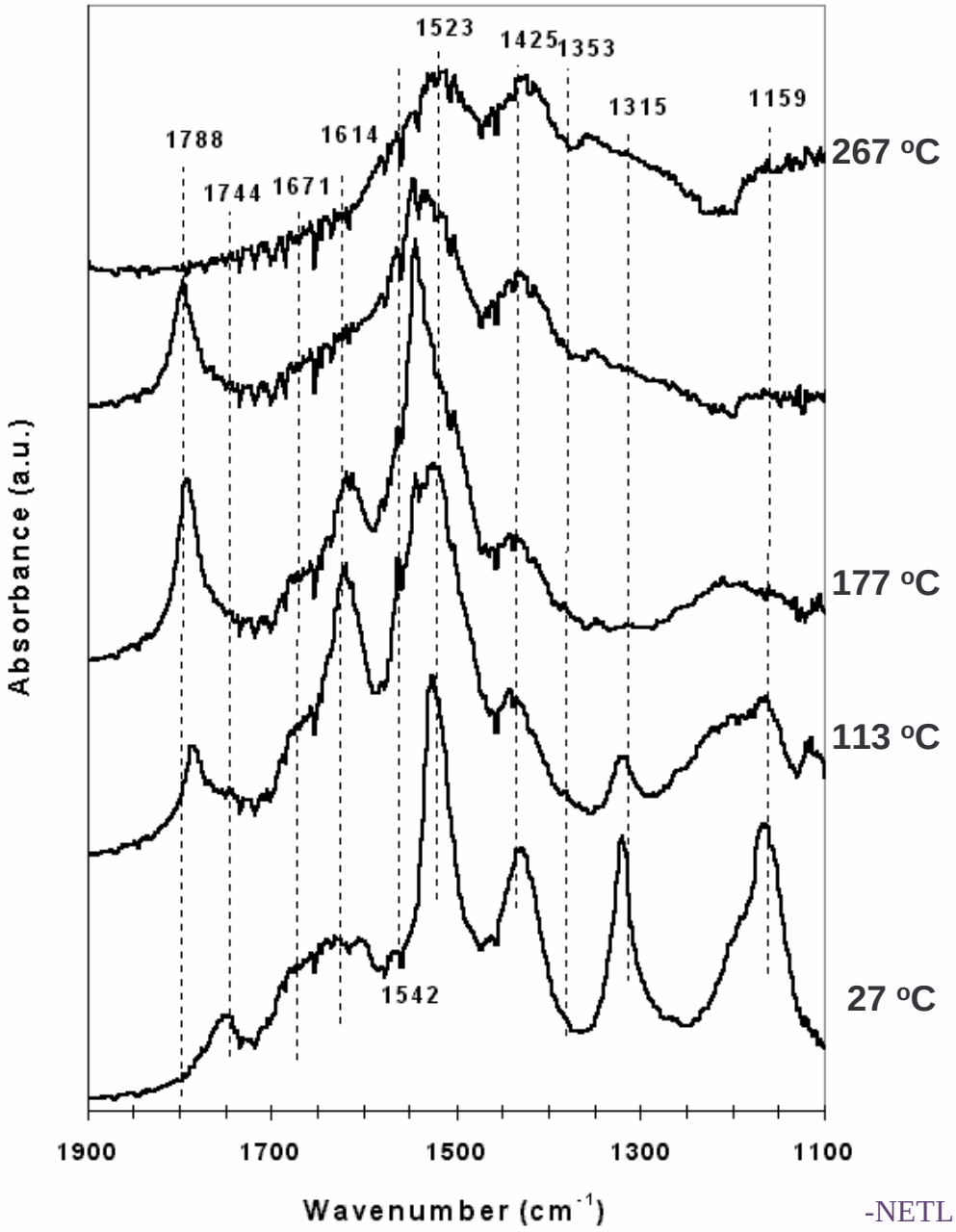
NO-TPD over Reduced Gd-Pd/TiO_2

- The band in 1740 - 1790 cm^{-1} region was more prominent over the Gd-Pd than Pd-only catalyst.
- The growing intensity of Pd-NO (1796 cm^{-1}) species with temperature could be due to decomposition / readsorption of monodentate nitrate (1522/1317 cm^{-1}), N_2O_4 (1744 cm^{-1}), and N_2O_2 (1163 cm^{-1}) species. This could explain the multiple NO desorption features observed in TPD experiments.
- Pd-NO, nitrate, and nitrito species remain on the surface at higher temperatures.



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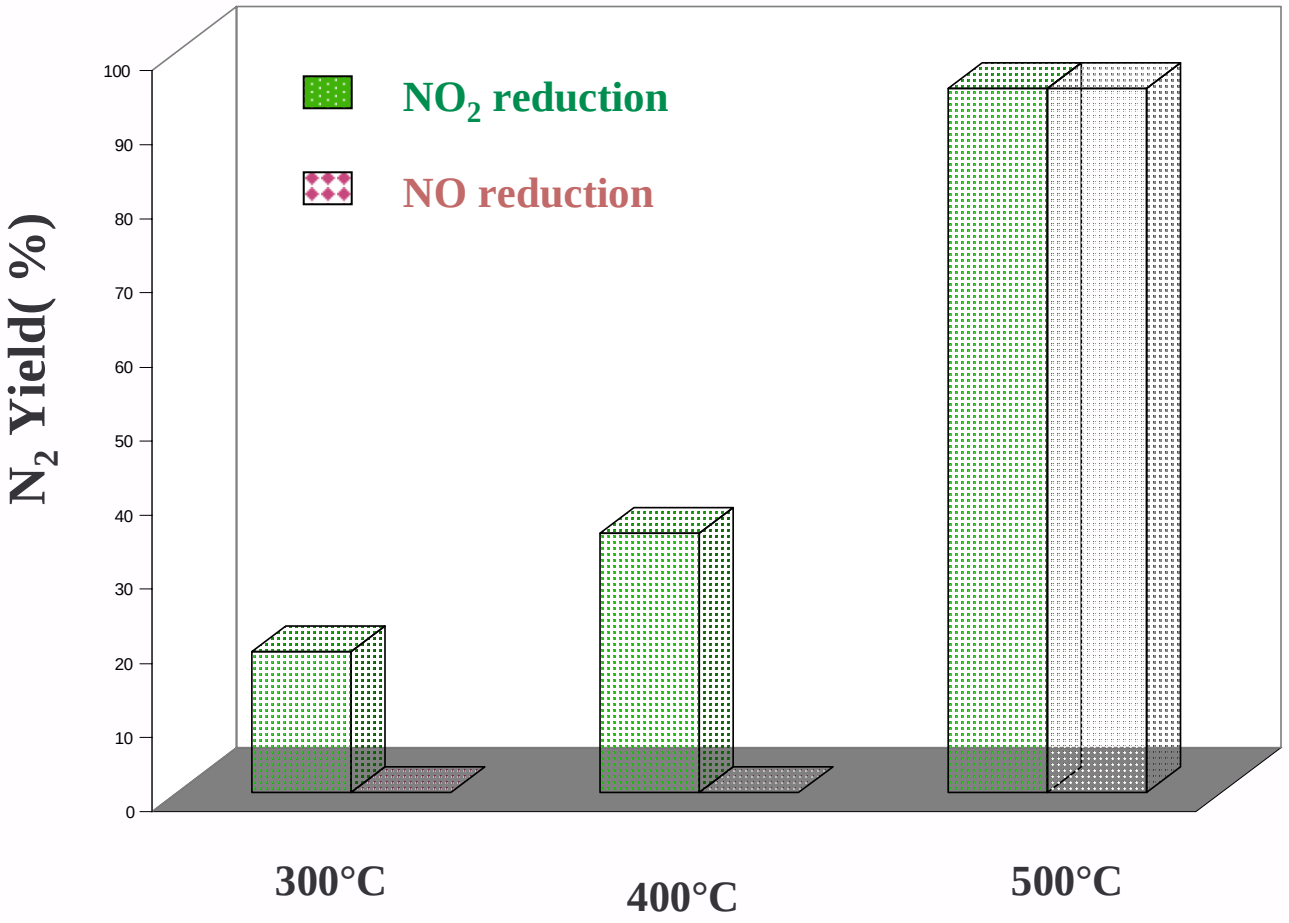
NO reduction versus NO_2 reduction



Gd-Pd-AC/TiO_2 catalyst, 500ppm NO_x, 10000 ppm CH_4, 2.5% O_2*

*2.3% O_2 for NO reduction

Initial Formulations for NO Oxidation Catalysts

Catalyst	Preparation	S.A. (m^2/g)
1%Ag/TiO_2	Modified sol-gel	5
3%Ag/TiO_2	Modified sol-gel	6
10%Ag/TiO_2	Modified sol-gel	27
1%Co/TiO_2	Modified sol-gel	TBD
3%Co/TiO_2	Modified sol-gel	TBD
10%Co/TiO_2	Modified sol-gel	40
1%Ce/0.1%Pd/TiO_2	Modified sol-gel	57
1%Ag-TiO_2/ZrO_2	Modified sol-gel	104
3%Ag-TiO_2 /ZrO_2	Modified sol-gel	65

Precursors: Titanium Isopropoxide, Zirconium Propoxide, Cobalt nitrate hexahydrate
Silver nitrate, Cerium nitrate, Palladium acetate, Gadolinium nitrate
Solvent is isopropyl alcohol

- Nitrogen is used as the adsorbate at liquid nitrogen temperature.
- The sample is degassed at 130 ^oC over night before the adsorption process is started.

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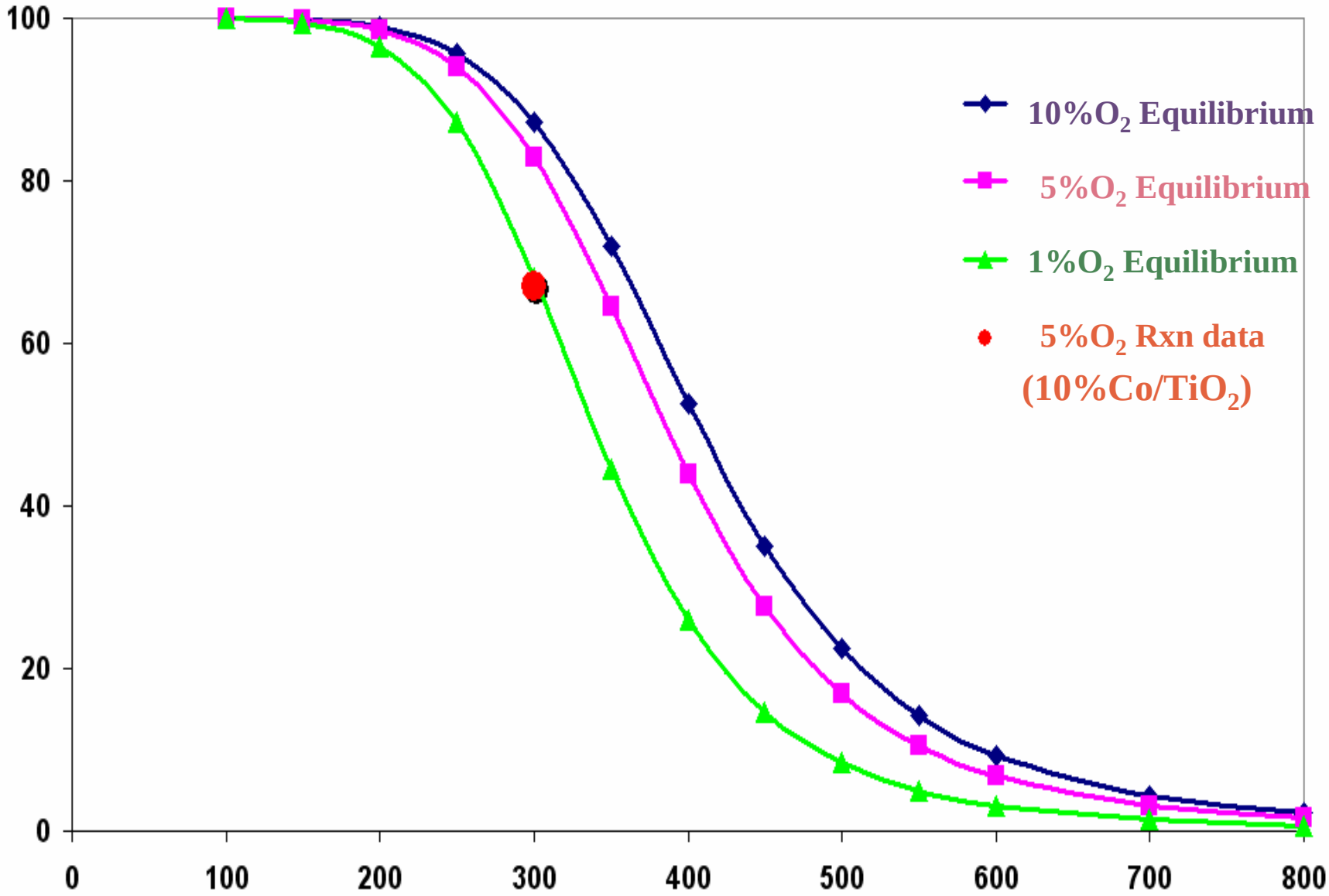

NO Oxidation (1000 ppm NO)

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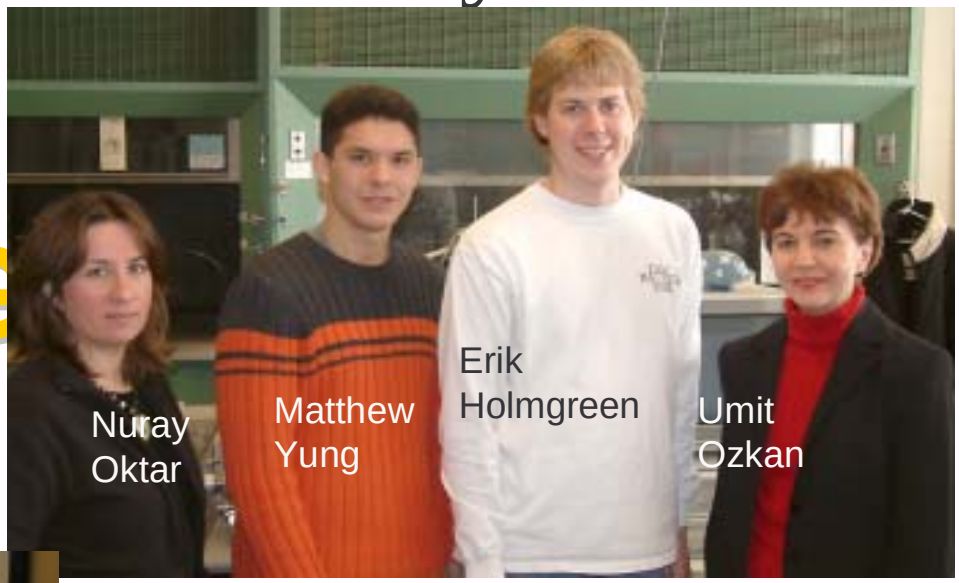
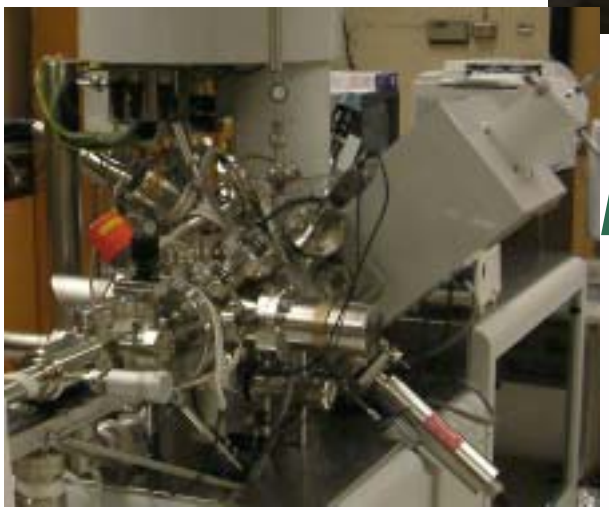
Heterogeneous Catalysis Research Group

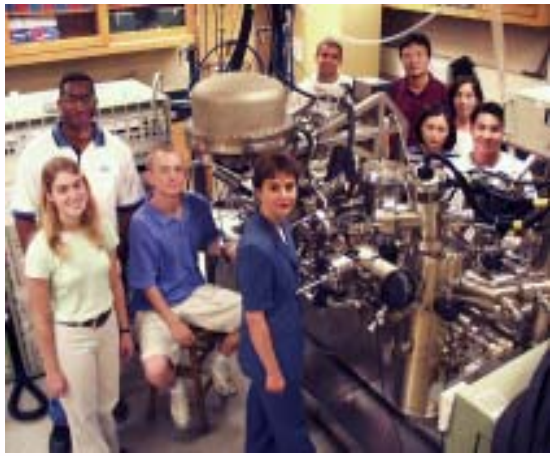




Energy

Environment

Economics



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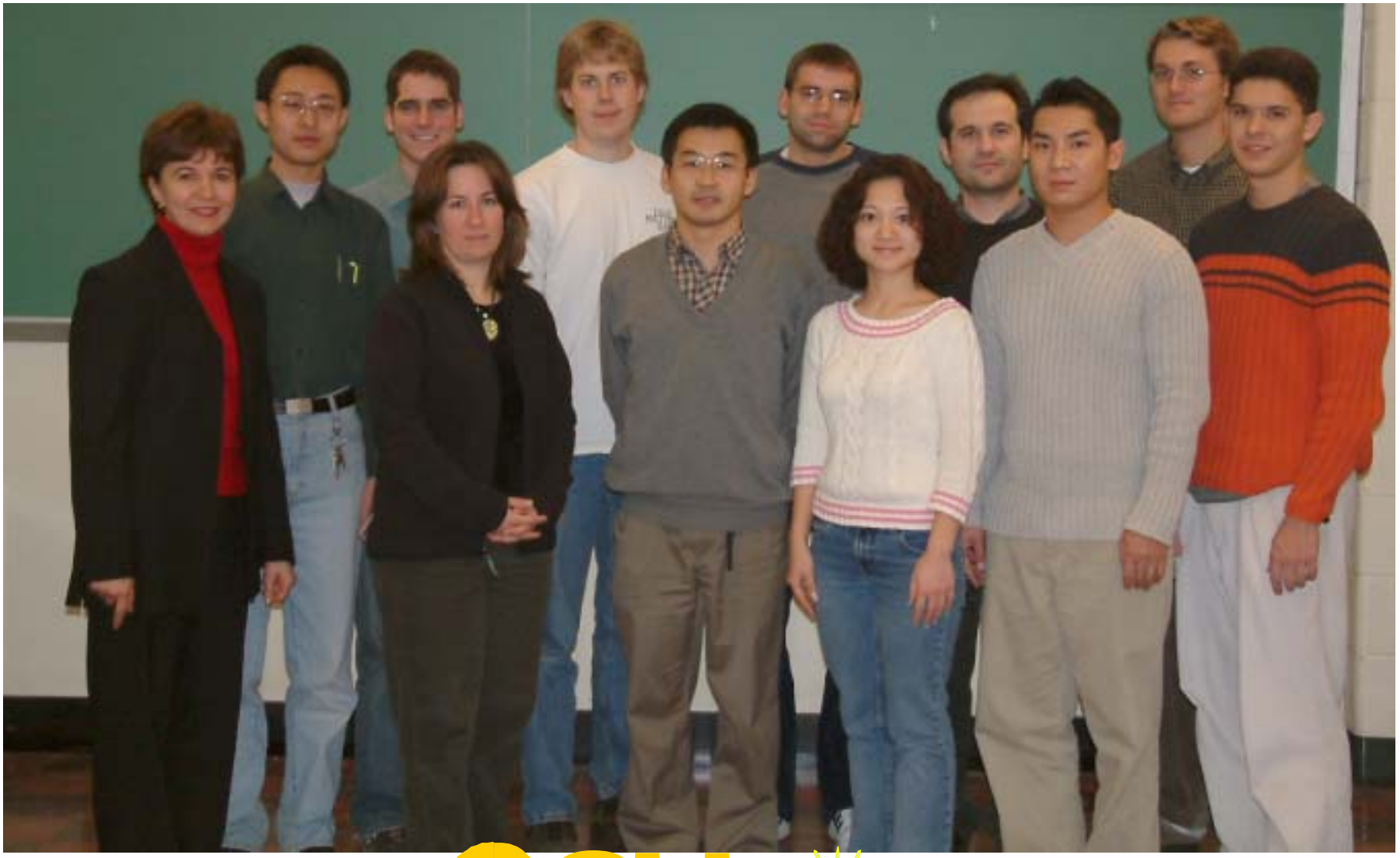

OSU Heterogeneous Catalysis Research Group HCRG

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Catalyst synthesis

To prepare catalysts with desired chemical and physical properties and to establish the relations between synthesis parameters and catalytic performance.

- Co-precipitation
- Impregnation/doping
- Calcination
- Carbiding
- Sulfiding
- Nitriding
- Reduction
- Activation
- Solid-state reaction
- Vapor deposition
- Controlled crystal growth
- Sol-gel synthesis
- Supercritical synthesis

Oxides

Sulfides

Nitrides

Supported metals

Heteropoly anions (collaborative effort)

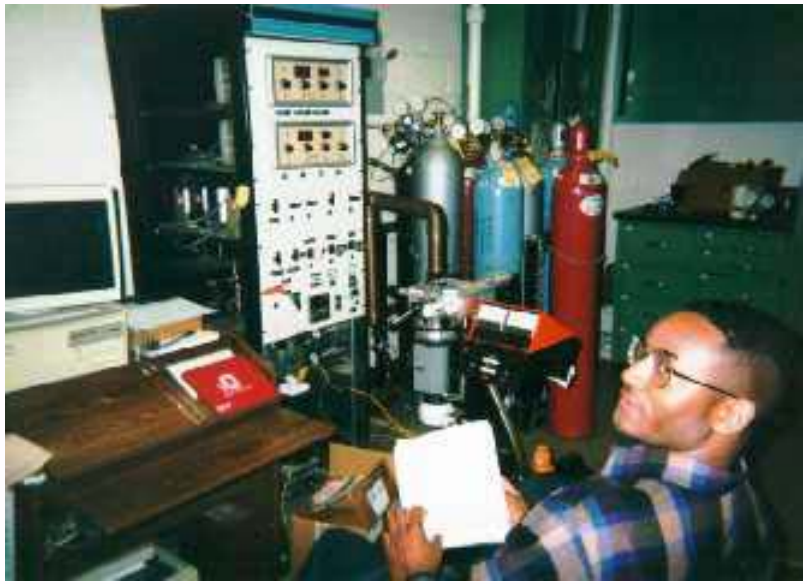
Intercalation compounds (collaborative effort)

Bi-metallic nano-particles (collaborative effort)

Reaction kinetics and reaction engineering

To examine the catalytic performance of the materials, to elucidate reaction schemes, to obtain kinetic parameters, and to establish relationships between the catalytic performance and the physical and chemical characteristics of the catalysts

- **Steady-State reaction experiments**
- **Transient-response reaction studies**
- **Kinetic measurements**
- **Isotopic labeling studies at transient and steady-state**
- **Isotopic labeling combined with *in-situ* vibrational spectroscopy**



Catalyst characterization

Using pre-reaction, post-reaction, controlled-atmosphere and in-situ analyses, to acquire in-depth information and fundamental understanding about physical and chemical characteristics of catalysts, including:

- surface area, pore size
- particle size/shape/morphology
- crystal structure
- chemical composition
- oxidation state
- molecular structure
- surface chemistry
- adsorption/desorption characteristics
- oxidation/reduction characteristics
- acidity/basicity

Catalysis "Toolbox"

❖Reaction experiments (micro or lab-scale reactors)

- Activity/selectivity
- Kinetic parameters
- Deactivation characteristics
- Mechanistic studies

❖Physical characterization

- Surface area
- Pore volume / pore size distribution
- Dispersion
- Particle size

❖Microscopy (SEM, TEM)

- Particle size / shape
- Dispersion
- Composition
- Surface morphology

❖Surface characterization

- X-ray Photoelectron Spectroscopy (XPS)
- Secondary Ion Mass Spectroscopy (SIMS)
- Auger-Electron Spectroscopy (AES)

❖Bulk and structural characterization

- X-ray Diffraction (XRD)
- X-ray Fluorescence (XRF)
- Energy Dispersive X-ray Analysis (EDXA)

❖Molecular and *in-situ* characterization

- Laser Raman Spectroscopy (LRS)
- Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)
- Nuclear Magnetic Resonance (NMR)
- Electron-spin Resonance (ESR)

❖Adsorption/desorption characterization

- Temperature Programmed Reduction (TPR)
- Temperature Programmed Oxidation (TPO)
- Temperature Programmed Desorption (TPD)

❖Thermal analysis

- Thermo-gravimetric Analysis (TGA)
- Differential Thermal Analysis (DTA)
- Differential Scanning Calorimetry (DSC)

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Summary

- The project is on schedule.
- Literature review, reactor modification, new equipment installation and testing have been completed, as planned.
- Initial catalyst formulations and reaction experiments provided proof of concepts proposed.
- NO_2 is shown to be more easily reduced than NO.
- Transition metal oxides can catalyze the NO oxidation.
- Detailed characterization studies are likely to provide the in-depth understanding needed to develop the catalytic system to achieve the proposed objectives.

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